Trace Metal and Nutrient Cycling in San Francisco Bay

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LONG TERM GOALS

The long term goals of this project are to examine the influence of metal flux (primarily Cu, Cd, As, Co, Mn and Fe) from sediments on the concentration of dissolved metals in the coastal zone and embayments. The processes that control trace metal exchange across the sediment-water interface within coastal environments regulate the concentration of dissolved, bioactive metals in the water column. These processes include variations in the relative influence of transport mechanisms (diffusion versus bio-irrigation), microbial activity (anaerobic versus aerobic respiration), as well as geochemical reactions (redox reactions, precipitation, complexation and adsorption) that regulate the behavior of dissolved metals in pore waters. All of these processes are controlled by the activity and composition of the sediment community. The role of organic carbon remineralization on trace metal mobility at a biologically active interface is, therefore, the focus of this study.

OBJECTIVES

Our long term objectives are to understand how sedimentary environments, which favor certain terminal electron acceptors (O_2, SO_4, Mn, Fe, etc...), affect the interaction between organic matter diagenesis and metal flux. Further, we must understand how the products and reactants of this diagenesis are transported between the sediments and the water column. In this study, measurements of carbon oxidation and metal flux are coupled with observations of dissolved metal concentrations in the water column to assess the strength of the sedimentary source. We have done this by coupling a study of organic matter diagenesis in sediments (W. Berelson, USC) with our measurement of metal flux across the sediment-water interface and vertical distribution of metals in sediment pore waters. We are extrapolating our study of the LA/Long Beach Harbor systems with a study of South San Francisco Bay.

In addition, we also included an objective to increase our understanding of the direct influence of benthic macrofauna, particularly the invasive species of Asian clam (*Potamocorbula amurensis*), on the flux of contaminant metals between the water column and sediments.

APPROACH

Our approach was to measure directly the benthic fluxes of trace metals (As, Cd, Mn, Co, Cu, Ni and Fe) and nutrients (oxygen, nitrate, ammonia, phosphate, silicate, TCO_2, alkalinity and ^{222}Rn) from

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sediments within San Francisco Bay utilizing benthic chambers. The depth distribution of these chemicals in the sediment was also to be determined in cores collected at the same sites where fluxes were measured. Our previous work has used benthic flux chambers designed for deep-sea deployments. In 1996, together with W. Berelson at USC, we developed a sea-floor incubation chamber that can be used more readily for environmental manipulation experiments in shallow systems. All of these measurements are accompanied by observations of dissolved metal concentrations in the water column. We have worked to develop an *in situ* chemical analyzer based on new digital pump technology, which is capable of conducting colorimetric analyses of both chamber and ambient waters. We have applied a stoichiometric approach to identify the importance of terminal electron acceptors and anoxic diagenesis in carbon remineralization, nutrient and metal release.

Our approach is to couple manipulative experiments of macrofaunal and microbial communities to assess their role in mediating chemical transport. The new chamber design allows for a variety of *in situ* operations. Manipulations involve the injection of oxygen (to assess the role of bottom water oxygen concentrations), acid (to determine the effects of changing pH), formaldehyde (to provide a diffusional control), molybdate (to quantify the role of sulfate reducing bacteria) and the addition of *Potamocorbula* clams into the chamber with concurrent sampling for chlorophyll and POC (to obtain measurements of biologically mediated particle removal).

WORK COMPLETED

In continuation of our LA/Long Beach Harbor Processes Studies, we have initiated our field efforts, now in San Francisco Bay. Our final field effort in South San Francisco Bay has just been completed in mid-September 1998. We have concentrated our current sampling at one site to allow a more coherent interpretation of the various measurements. During this last field endeavor, we deployed and recovered 6 benthic chambers. These deployments included chamber manipulations which involved incubation of the same seafloor footprint in the presence and absence of added *Potamocorbula* clams, the addition of formaldehyde, as well as a small arsenic spike to look at As speciation. Filters were added to the time series sampling apparatus to collect samples for POC, PON and chlorophyll. In addition, we have recovered 7 cores from the site, two of which were taken from inside the chamber deployment footprint. Both chamber waters and sediment pore waters are undergoing analysis for metals (Cd, Cu, Co, Mn, Ni, AsII, AsIV), nutrients (NO_3, Si, PO_4) bromide, and sulfide (J. Kuwabara, USGS).

RESULTS

Results from comparisons of both new and old style chambers indicate that both produce the same results. Although the samples from the current field effort have yet to be analyzed, results from previous San Francisco deployments, together with those of the LA/Long Beach Harbors, demonstrate the importance of dissolved metal fluxes from sediments in regulating the concentration of dissolved, bioactive metals in the system. The results of the manipulative experiments demonstrate the importance of understanding the processes that control flux. Injecting metabolic inhibitors causes a dramatic decreases in metal flux, which indicates the importance of microbial remineralization in regulating metal flux. However, organic carbon remineralization alone is not the most important factor in regulating flux. The role of benthic macrofauna as the gatekeepers of material transport (POC, trace metals and nutrients) between the water column and the sediments need also be addressed. With the current sampling effort and manipulative chamber experiments we hope to characterize our deployment sites with respect to macrofauna biomass and behavior (filter feeding, surface feeding or burrowing) and relate these findings to trace metal flux, particle removal, depth and rate of tracer transport.

IMPACT

Our results will directly impact the consideration of sediment decontamination measures. We have identified the sediments as sources for some metals and a sink for others, the sign depends upon the macrofauna and microbial activity. Although this is a more complicated picture, it has the potential to be exploited selectively where mobilization or preservation of a particular contaminant is desired.

In this new environment, with these new capabilities, we have been able to perform some very novel experiments. For example, San Francisco Bay has been infested with the Asian Clam (*Potamocorbula amurensis*). This voracious filter feeder made its way here in the ballast of ships in 1984 and now controls the blooms of phytoplankton in the Bay. We have been engaged in discussions with researchers from USGS who are well acquainted with the biology of this organism, but we believe there is an important geochemical side to this story as well. We believe that the Asian clam plays an important role in actively transporting particulate organic carbon (and elements adsorbed to these particles) from the water column to the sediments, thereby affecting not only the rate of POC transport, but the diagenetic environment downcore, and the resultant flux of dissolved constituents (trace metals and nutrients) from the sediments. This is but one organism that may serve to mediate the transport of materials from the water column to the sediments and back. Other macrofaunal invertebrates, many of which are also invasive species, also function as the gatekeepers of transport. Our current sampling effort may enable us to clarify the role of Potamocorbula in this transport mechanism.

This project has significant impacts for our understanding of the behavior of metals in coastal systems. It allows us to separate the natural and anthropogenic processes that both lead to elevated metal concentrations in embayments. More new studies with benthic macrofauna will allow for emerging hypotheses of metal accumulation and transport to be directly assessed with environmental measurements under relevant flow conditions.

TRANSITIONS

As we move our research from low energy boundary layers into high energy boundary layers, both the role of macrofauna become more pronounced and reproduction of the hydrodynamic regime becomes more important. In the deep-sea, passive particle settling determines POC delivery to the sediments. In areas heavily populated by macrofauna, their behavior also plays a major role in POC flux. Whereas the current stirring bars within the chambers reproduce the boundary layer of the deep-sea environment, there is some evidence to suggest that the advective conditions of the environment, within the chamber, is an important factor which may regulate the rate at which macrofauna filter-feed/bioirrigate, and thus move both solute and particulate phase materials between the water column and underlying sediments.

RELATED PROJECTS

Both the California Department of Fish and Game (CDFG) and the United States Geological Survey/Water Resources Division (USGS/WRD) have keen interest in the cycling of contaminant metals and the role of benthic macrofauna in the Bay (especially the invasive species such as

Potamocorbula) but have no direct way to assess the flux of these contaminants between the water column and the sediments. Our measurements will compliment the studies being undertaken by these agencies. We have collected samples of pore waters for Dr. James Kuwabara (USGS/WRD) for the analysis of acid volatile sulfur species (AVS). AVS has been shown to be a proxy for excess metal binding potential of pore waters and an indicator of toxicity. We intend to correlate these measurements with those of metal flux and metal porewater profiles in the interpretation of our results. We have initiated a study of the potential role of benthic macrofauna in collaboration with Dr. Jan Thompson (USGS/WRD) and are working with her to improve the chamber design as pertaining to the boundary layer. There is some emerging evidence that *Potamocorbula* may also play a role in mercury cycling as well. Mark Stephenson (CDFG) received samples from us for measurements of mercury cycling at the sediment/seawater boundary.

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